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**Precision Estimates for EPA Test
Method 8 - SO₂ and H₂SO₄ Emissions
from Sulfuric Acid Plants**

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PRECISION ESTIMATES FOR EPA TEST METHOD 8— SO₂ AND H₂SO₄ EMISSIONS FROM SULFURIC ACID PLANTS

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Abstract—The results from a collaborative test of the U.S. Environmental Protection Agency Test Method 8 are presented. In the collaborative test six laboratories simultaneously sampled the same stack at a sulfuric acid plant using two Method 8 sampling trains per laboratory. The collaborative test determined that the repeatability of the method was 7.61 mg sulfuric acid per m³ and 22.30 mg sulfur dioxide per m³. Similarly, the reproducibility of the method was 8.43 mg sulfuric acid per m³ and 31.10 mg sulfur dioxide per m³. The estimates of precision were determined to be independent of the pollutant concentration over the concentration range measured.

INTRODUCTION

Test Method 8 is the U.S. Environmental Protection Agency reference method for determining the sulfuric acid mist and the sulfur dioxide emissions from sulfuric acid plants (Environmental Protection Agency, 1971), and is also widely used by state and local governments throughout the world. In this method, the sampled stack gas is first passed through an isopropyl alcohol solution and then a filter to collect the sulfuric acid mist and then into a hydrogen peroxide solution to collect the sulfur dioxide. The amount of sulfate collected is then determined by titration with barium perchlorate using thorin as the indicator.

The first collaborative test of Method 8 was done at a sulfuric acid plant in St. Louis, Missouri in October, 1973. This test showed that the analytical portion of the method was accurate and precise, but the sampling portion was not (Hamil, 1974). In this first collaborative test four laboratories each independently but simultaneously, sampled the same stack using their own Method 8 sampling trains. (At any one time, each laboratory was sampling through a different port, but each laboratory achieved a complete sampling run by performing a radius traverse through each of the four ports.)

A study was then done to determine the reasons for the poor precision in the sampling part of the method. Two major sources of error, both of which could have occurred in the collaborative test, were found (Knoll, 1977). First, reagent grade isopropyl alcohol sometimes contains organic peroxides that would convert sulfur dioxide to sulfate. Second, if the filter is

wetted with hydrogen peroxide reagent during the leak-check, sulfur dioxide could be converted to sulfate on the filter.

Thus, it was decided to conduct another collaborative test of Method 8, but this time to impose strict quality assurance procedures on the test equipment, reagents, and operator techniques. This second collaborative test was done at a sulfuric acid plant in Mulberry, Florida using Method 8 as revised in August 1977 (Environmental Protection Agency, 1977).

DESIGN AND CONDUCT OF THE SECOND COLLABORATIVE TEST

The test design, equipment specifications, participant selection procedures and quality assurance procedures used in this collaborative test and the reasons for using them are essentially the same as those previously employed in a collaborative test of EPA Test Method 13 (Mitchell, 1977). Thus, these procedures will only be summarized here and readers wishing a more detailed discussion should consult the above reference.

In the second collaborative test of Method 8, the six participating laboratories simultaneously sampled the same stack using two Method 8 sampling trains each. This was accomplished by using three sampling clusters; each cluster was composed of two laboratories, two "S" type pitot tubes and four sampling trains (two trains per laboratory) with the nozzle tips located at the corners of a 5 cm square. Within a cluster, each laboratory used its own pitot tube to

Table 1. Laboratory pairings in the collaborative study of EPA Test Method 8

Day	Run	Sampling cluster		
		1	2	3
1	1	101, 102	103, 104	105, 106
	2	101, 103	102, 105	104, 106
2	3	101, 104	103, 105	102, 106
	4	101, 105	103, 106	102, 104
3	5	101, 106	104, 105	102, 103
	6	101, 102	103, 104	105, 106
4	7	101, 103	102, 105	104, 106
	8	101, 104	103, 105	102, 106

maintain isokinetic sampling rates in its two trains. Each cluster achieved a complete sampling run by performing a radius traverse at each of the four sampling ports. However, at any one time only one cluster was sampling through a specific port and all three clusters rotated between ports at the same time. The pairing of the six laboratories was changed between sampling runs so that every laboratory was paired-up with every other laboratory at least once (Table 1). Leak-checks were conducted before sampling was initiated, before and after each port change, and at the conclusion of each sampling run. At the end of each sampling run, the sampling trains were purged for 15 min with charcoal-filtered ambient air as required in Test Method 8. In this way, two, 2-hour long sampling runs were accomplished each day in a 10-hour time span.

RESULTS AND STATISTICAL ANALYSIS

The sulfuric acid mist and the sulfur dioxide results reported by the collaborators are presented in Tables 2 and 3.

When these results were subjected to a test for outliers, two sulfuric acid mist values (samples 2A and 7A) and two sulfur dioxide values (samples 2A and 5B) reported by Laboratory 101 were identified as statistical outliers. These outliers were omitted without replacement from the subsequent analysis of variance (ANOVA) performed on the collaborative test results.

Before performing the ANOVA, the data were examined to be sure they met the assumptions that underlie the ANOVA procedure. For example, the standard deviation for each run was examined and found to be independent of the pollutant concentration and the variances were determined to be homogeneous.

The ANOVA used the following linear model to describe the test results for each pollutant:

$$x_{ijk} = \mu + R_i + L_j + RL_{ij} + E_{k(i,j)}$$

where:

x_{ijk} is the k th observation during run i by laboratory j ;

Table 2. H_2SO_4 results from the collaborative study of EPA Test Method 8 ($mg H_2SO_4/m^3$)

Run	Sample No.	Laboratory					
		101	102	103	104	105	106
1	A	7.8	9.7	6.4	9.1	8.6	6.9
	B	11.5	7.8	6.7	8.8	7.8	13.2
2	A	166.0*	6.2	4.1	5.2	4.3	6.5
	B	6.4	4.5	4.0	5.9	7.8	11.5
3	A	6.8	6.1	5.2	7.3	†	9.9
	B	2.9	†	4.6	5.9	6.1	2.6
4	A	9.9	4.8	6.3	8.3	11.0	9.8
	B	5.4	6.9	7.1	6.2	5.2	12.6
5	A	6.9	7.2	7.9	8.6	5.4	14.9
	B	17.8	15.2	9.4	12.3	5.1	10.7
6	A	6.7	7.1	6.9	6.8	10.1	12.4
	B	3.6	8.0	6.6	9.6	7.8	8.3
7	A	43.0*	7.6	9.9	13.2	11.8	11.8
	B	8.5	9.9	8.3	8.1	9.5	15.4
8	A	9.7	8.3	8.3	12.7	7.0	12.4
	B	7.6	11.0	6.4	21.9	10.9	12.5

* Outlier - not included in any further analysis.

† Sample lost.

μ is the population average;

R_i is the run effect, exemplifies a random fluctuation in concentration due to sampling over different time periods, that is, runs ($i = 1, 2, \dots, 8$);

L_j is the laboratory effect, random because laboratories were randomly selected to participate in the test ($j = 1, 2, \dots, 6$);

RL_{ij} is the run by laboratory interaction term;

$E_{k(i,j)}$ is all other random errors not accounted for by the above design.

Table 3. SO_2 results from the collaborative study of EPA Test Method 8 ($mg SO_2/m^3$)

Run	Sample No.	Laboratory					
		101	102	103	104	105	106
1	A	147	153	163	163	159	156
	B	154	155	155	143	153	167
2	A	77*	200	191	205	189	195
	B	196	197	189	196	196	202
3	A	194	194	179	187	†	194
	B	192	†	191	187	†	200
4	A	291	288	300	296	290	286
	B	286	290	300	285	283	303
5	A	278	286	298	290	291	281
	B	565*	291	296	290	270	292
6	A	278	286	309	295	294	302
	B	293	293	308	312	291	288
7	A	251	220	295	287	288	277
	B	282	258	292	290	280	283
8	A	274	288	291	274	261	280
	B	282	278	293	282	256	285

* Outlier - not included in any further analysis.

† Sample lost.

In this model, which is based on one described by Searle (1971), all the above effects are considered to be random with long-term averages of zero and variances σ_R^2 , σ_L^2 , σ_{RL}^2 and σ_E^2 , respectively. In other words, the total variation of an observation is assumed to be a linear combination of the above components expressed as:

$$\sigma_z^2 = \sigma_R^2 + \sigma_L^2 + \sigma_{RL}^2 + \sigma_E^2.$$

The estimates for these variance components are contained in Table 4 along with the estimates of the within-laboratory precision (repeatability) and the between-laboratory precision (reproducibility). For our purposes repeatability and reproducibility are defined here according to Mandel (1971). That is, repeatability, $2.77\sigma_R$, is defined as the absolute difference between two observations made by the same laboratory on the same sample that would be exceeded only five percent of the time due to chance alone. Similarly, reproducibility, $2.77(\sigma_R^2 + \sigma_L^2 + \sigma_{RL}^2)^{1/2}$, is defined as the absolute difference between observations made by two different laboratories on the same sample that would be exceeded only five percent of the time due to chance alone.

DISCUSSION OF RESULTS AND CONCLUSIONS

The results from the second collaborative test of EPA Test Method 8 showed that the overall precision of the test method is good if sound quality assurance procedures are observed during testing. For example, quality assurance on the second collaborative test was improved from the first collaborative test in the following ways: (1) the orifice and dry gas meter calibration coefficients of all control consoles used were checked on-site with a dry gas meter that had been calibrated with a spirometer; (2) prior to the test all reagent isopropyl alcohol was certified to be peroxide-free (Knoll, 1977); (3) leak-checks were done at the beginning and at the end of each sampling run and before and after every port change; and (4) care was taken to ensure that the sulfur dioxide absorbing reagent, hydrogen peroxide, did not contact the filter when the leak-check was done (if peroxide did contact the filter, the filter was replaced before sampling was continued).

Compared to the first collaborative test (Hamil, 1974), the result of employing the above quality assurance procedures was a sharp improvement in the

quality of the data obtained, that is, only 2 percent of the values reported were identified as outliers. Further, by using paired-sampling trains and paired-laboratories, it was possible to certify that a result was a true outlier by comparing it with the results from the three other sampling trains in that cluster.

Although care was taken to ensure that hydrogen peroxide did not contact the filter, the test data indicate that at least two of the four outliers -- the values for acid mist and sulfur dioxide obtained by Laboratory 101 on sampling train A in run 2 -- likely resulted from this type of error. Further, comparison of the average results reported for each cluster in each run to those reported for the other clusters in that run, make it apparent that spatial and temporal variations in the pollutant profile did not contribute significantly to the precision estimates obtained.

The estimate of the within-laboratory precision in the acid mist measurement obtained here is statistically identical to one determined in a single laboratory evaluation of Method 8 done at another sulfuric acid plant (Mitchell, 1974). (In this latter study a single laboratory operated four sampling trains simultaneously using a sampling cluster identical to that used here.) Since the acid mist concentration encountered in the single laboratory study was four times higher than that encountered here, the similar precision estimates indicate that the within-laboratory precision is not a function of the pollutant concentration. Thus, it is not appropriate to express the acid mist precision as a function of the mean.

Also, following statistical convention, the precision estimates in Table 4 apply to the expected differences between single measurements and not averages.

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Table 4. Precision estimates for EPA Test Method 8

Variance component	H ₂ SO ₄	SO ₂
σ_R^2	3.13	3114.94
σ_L^2	1.71	14.52
σ_{RL}^2	0.0	46.73
σ_E^2	7.55	64.81
Repeatability	7.61 mg H ₂ SO ₄ /m ³	22.30 mg SO ₂ /m ³
Reproducibility	8.43 mg H ₂ SO ₄ /m ³	31.10 mg SO ₂ /m ³

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